

RAW MATERIALS

UDC 666.1:666.3:553.623.54(476)

GLAUCONITE MATERIALS FROM BELARUS AND THEIR APPLICATION PROSPECTS

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An integrated study of glauconite-bearing rocks of the Republic of Belarus has been performed and their main application directions have been identified. The chemical, mineral, and granulometric compositions of these rocks are studied and some of their physicochemical and technological properties are analyzed.

Glauconites are dense sedimentary rocks of dark green, sometimes greenish-black color and low hardness, belonging to the ferrous hydromica group according to their mineral type. The investigation of glauconite and glauconite-bearing rocks for the purpose of using them in the production of silicate materials is important in the context of integrated application of these minerals and the need for developing new natural resources for the industry, and also in view of insufficient knowledge of their technological properties.

Glauconite materials in the Republic of Belarus are represented by polymict glauconite sands with a high content of the quartz component and occur in the central and southern regions of the republic. Glauconite beds occur at a small depth and belong to the Upper Cretaceous and Paleocene deposits. According to the data of the Institute of Geology of the National Academy of Sciences of Belarus [1, 2], the most promising are the southern and south-eastern deposits of glauconite (Dobrushskii, Loevskii, Stolinskii, and other districts).

We have investigated natural and concentrated glauconite-bearing rocks from the Dobrush (Gomel Region) and Karpovtsy (Grodno Region) deposits. We have analyzed the structure, mineralogical specifics, and phase transformations under heat treatment of rocks from 20°C to their melting.

Glauconite-bearing rocks of the Karpovtsy deposit are sedimentary rocks, light green or green with a yellowish-gray shade, whose main component is quartz: 70 – 82% (here and elsewhere wt.%). Impurity inclusions are represented by potassium-sodium feldspars up to 2%. They are found in the sands in the form of grains with diameters from one to several millimeters. The glauconite content is not higher than 23%.

Glauconite-bearing rocks of the Dobrush deposit have a more saturated green color and a diverse mineral composition. The quartz content is 85 – 93%, feldspar 2 – 3%, argillaceous impurities in the form of muscovite, biotite, and illite 3 – 4.5%. The glauconite content varies from 5.5 to 19.0%, and the mean content is 12.0%.

The specified rocks after concentration are represented mainly by glauconite and have a saturated dark green, nearly black color. The results of x-ray phase analysis of the rocks are given in Fig. 1.

Glauconite sand are characterized by a substantial quantity of silicon oxide (70.36 – 89.73%), aluminum oxides (2.72 – 11.15%), and iron oxides (II, III) 3.22 – 9.20%, as well as oxides of alkali and alkaline-earth metals (2.90 – 7.12%). Upon concentration, the quantity of iron oxides (II, III) in the rock increases and is equal to 21.78 – 25.50%. The content of silicon oxide decreases to 49.45 – 54.10%. The chemical composition of glauconite-bearing rocks is presented in Table 1.

According to the sieve analysis, the majority of particles, namely 52.50 – 84.20% has grain size from 0.10 to 0.63 mm. The share of coarse particles is not more than 1.5%. The content of particles of size below 0.63 mm, which depends on the sand content of the glauconite-bearing rock, in Karpovtsy rock is 35.20 – 47.20% and in Dobrush rock 12.20 – 19.36%.

The results of the analysis obtained using an ASTA-2 automatic plant indicate that the glauconite-bearing rocks have a polydisperse composition including particles of diverse shapes with sizes ranging from fractions of a millimeter to tens and hundreds of millimeters. Regardless of the depth of sampling, the rock includes large particles of size 150 – 200 μm , crystals 40 – 100 long and 10 – 30 μm wide,

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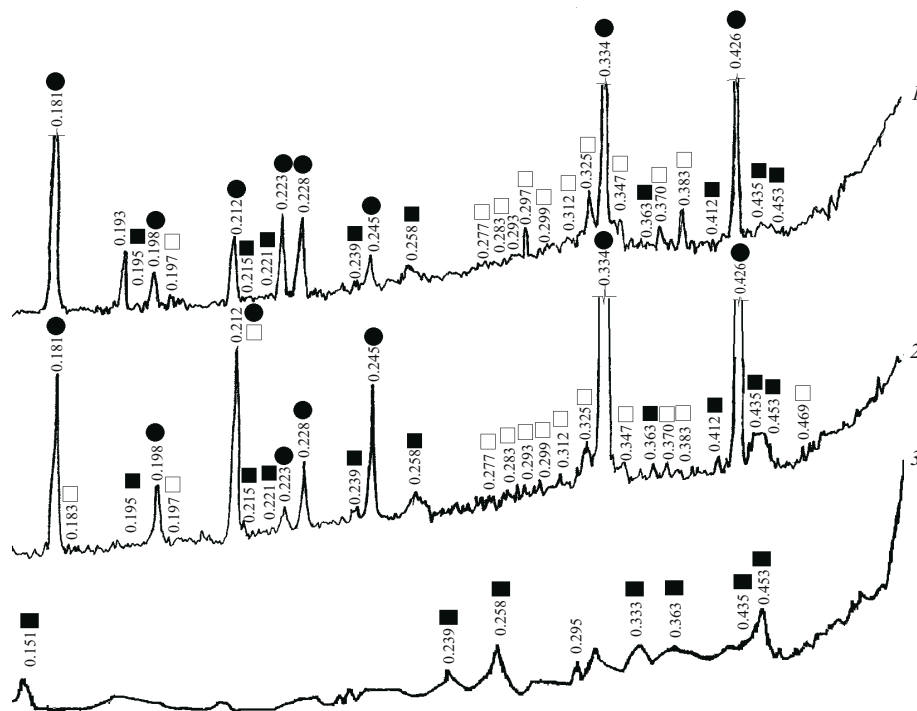


Fig. 1. Diffraction patterns of glauconite-bearing rocks from Dobrush (1) and Karpovtsy (2) deposits and concentrated glauconite (3): ■ glauconite; □ feldspar; ● quartz.

spheroid particles of diameter 5–10 μm , and their agglomerates of size 60–90 μm . The content of the 0–15 μm fraction is 7.0–9.0%. It is established that samples of glauconite-bearing sands after heating within a temperature range of 400–800°C have larger particles, which is a consequence of their conglomeration under heat treatment.

The bulk density of glauconite-bearing rocks depending on quartz sand content varies from 1392 to 1572 kg/m^3 . The unit effective radioactivity does not exceed the existing regulations for the content of radioactive agents in natural materials (370 Bq/kg) and is equal to 67.8–94.5 Bq/kg.

Differential-thermal analysis was performed in the temperature interval of 20–1150°C for the purpose of studying the specifics of phase and structural transformations of glauconite-bearing rocks and concentrated glauconite in firing. Multi-position thermal treatment was carried out in the temperature interval of 1000–1300°C with a temperature

variation step of 100°C and 60-min exposure at each temperature.

According to the DTA data, the endothermic effects upon heating glauconite in the temperature intervals of 55–210 and 430–680°C are related to the removal of adsorption (mechanically bound) and hydroxyl (chemically bound) water, respectively. The exothermic effect at the temperatures of 330–370°C is due to the oxidation of structural iron (II) and its transition to the trivalent state. The process of hematite formation in the temperature interval of 700–970°C proceeds simultaneously with the removal of the second portion of water. The derivatograms of natural glauconites additionally exhibit effects corresponding to the phase transformations of quartz. The total weight loss in the calcination of natural rocks is equal to 2.0–4.4% and in concentrated rocks 8.8–11.4%.

According to x-ray phase analysis data, the destruction of the crystalline structure of glauconite occurs immediately after the loss of chemically bound

water. As the firing temperature increases, hematite, which is formed in heating, partly transforms into wustite FeO with the formation of iron-bearing solid solutions, namely, magnesium aluminoferrites whose compositions range from $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ and $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ to $(\text{Mg}, \text{Fe})\text{Al}_2\text{O}_4$. It is worth noting that in firing glauconite sand, fayalite is formed in the temperature interval of 1100–1200°C and after the temperature grows above 1200°C cristobalite is formed. The dependence of the intensity of the main crystalline phases on firing temperatures of concentrated glauconite is shown in Fig. 2.

It can be seen from the data of Table 2 that samples of concentrated glauconite sinter at temperatures around 1100°C and melt in the temperature interval of 1150–1200°C. The color of the samples with increasing firing temperature changes from red-brown to black. Swelling of samples is observed at a temperature of 1200°C. The temperature

TABLE 1

Rock sample	Weight content, %											
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	MnO	K_2O	Na_2O	P_2O_5	SO_3
Dobrush deposit	83.31 –	0.24 –	2.72 –	3.22 –	0.46 –	0.77 –	0.82 –	0.00 –	1.17 –	0.14 –	0.02 –	0.60 –
	89.73	0.36	4.72	4.87	0.73	1.55	1.11	0.05	1.99	0.20	0.20	1.02
Karpovtsy deposit	70.36 –	0.60 –	9.07 –	7.11 –	0.46 –	0.35 –	2.43 –	0.05 –	3.61 –	0.38 –	0.02 –	0.04 –
	76.38	0.67	11.15	9.20	0.73	0.54	2.48	0.09	3.64	0.37	0.17	0.10
Concentrated glauconite	49.45 –	0.98 –	8.74 –	19.54 –	2.24 –	2.22 –	3.62 –	0.04 –	4.77 –	0.25 –	0.10 –	0.11 –
	54.10	1.10	12.46	23.29	4.60	1.19	2.33	0.09	6.52	0.99	0.58	0.69

TABLE 2

Firing temperature, °C	Characteristics of rocks	
	glaucanite sand*	concentrated glaucanite
1000	Sample of red-brown color, friable, liquid phase is absent. Main crystalline phases: quartz, hematite, feldspars	Symptoms of the formation of liquid phase are registered. A low-strength cake is formed that easily disintegrates under mechanical impact. Dark brown color. Main crystalline phases: hematite, magnetite
1100	Loose structure, intense red-brown color of the rock. Main crystalline phases: quartz, hematite, feldspars, fayalite	Sintering of sample is registered, vitreous luster, dark brown color. Dense structure, although the formation of sealed pores up to 0.5 mm is registered over the whole volume. (porosity is due to the reduction of iron oxides). Main crystalline phases: hematite, magnetite
1200	Low-strength cake is formed, symptoms of the formation of the liquid phase are observed. The color changes to brown. Main crystalline phases: quartz, hematite, feldspars, fayalite, magnetite, cristobalite	The rock melts, the structure of the sample is porous, inhomogeneous color changing from brown to black. Vitreous luster. Main crystalline phases: hematite, magnetite
1300	Vitrified cake of black color, strong. Main crystalline phases: quartz, magnetite, cristobalite	Complete melting and swelling of sample, black color, vitreous luster. Main crystalline phase: magnetite

* No significant differences were registered between the behavior of glaucanite-bearing rocks from Karpovtsy and Dobrush deposits under heating.

of glaucanite sand sintering is 100 – 200°C higher than that of concentrated glaucanite.

The IR-spectroscopy analysis of concentrated glaucanite indicates that despite the complexity of its chemical composition, this material, similarly to other laminated silicate (for instance, biotite), has an intense absorption band in the interval of 1170 – 1100 cm^{-1} related to the valence vibrations of Si – O and Si – O – Al(IV) links and a few weaker bands in the range of 800 – 780 cm^{-1} related to the vibrations of Si – O – Si and Al(IV) – O bonds. The bands at 620 – 560 cm^{-1} relate to the vibrations of Al(VI), Mg(VI), and Fe(VI) – O and the bands at 560 – 440 cm^{-1} to the deformation vibrations of Si – O – Me²⁺ (Me³⁺) links [3]. The spectrum of the investigated glaucanites has no OH-band, which is presumably due to the existence of weak hydrogen links. In heating glaucanite, the form of the spectra persists; as the Fe²⁺:Fe³⁺ ratio varies, the bands at 588 – 585 and 516 – 512 cm^{-1} become somewhat intensified. The shift of these bands by 5 – 8 cm^{-1} is presumably caused by the replacement of Fe²⁺ in the structure of the compounds by Mg²⁺ and by the growing quantity of the vitreous phase in the analyzed sample [3].

The results of analysis of the chemical, granulometric, and mineral compositions of the considered rocks and concentrated glaucanite support the advisability of using them in ceramic mixtures for wall ceramics, wall and floor tiles, majolica, etc. Due to the high content of free quartz in these rocks, they can be simultaneously used as the fluxing component (glaucanite) and the grog component (quartz) in ceramic mixtures, as well as additives ensuring volumetric tinting of products due to an enhanced content of colorant oxides. The high content of iron and alkali metal oxides in glaucanite can presumably intensify the sinterability of ceramic mixtures and ensure prescribed physicochemical cha-

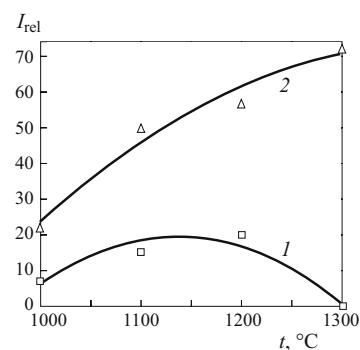


Fig. 2. Dependence of intensity of main crystalline phases on glaucanite firing temperature: 1) hematite; 2) magnetite.

acteristics of materials due to the formation of a low-viscosity melt and the required crystalline phases under thermal treatment below 1100°C.

The presence of the colorant iron oxides in glaucanite-containing rocks makes then suitable for the development of glasses and vitreous coatings with a wide color range without additional introduction of colorant components. Such rocks can at the same time be a source of quartz material. Concentrated glaucanite, after adding corresponding additives, can be used to produce ceramic pigments, tinted glazes, stone casting, and rock glass ceramics.

REFERENCES

1. *Mineral Resources of Belarus* [in Russian], Adukatsia i Vykho-vanne, Minsk (2002).
2. L. I. Murashko, "Glaucanite in paleogenic deposits of Belarus," *Litosfera*, No. 4, 111 – 119 (1998).
3. I. I. Plyusnina, *Infrared Spectra of Silicates* [in Russian], Izd-vo MGU, Moscow (1967).